

Pyridine intercalated Bi_2Se_3 heterostructures: controlling the topologically protected states

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We use *ab initio* simulations to investigate the incorporation of pyridine molecules ($\text{C}_5\text{H}_5\text{N}$) in the van der Waals gaps of Bi_2Se_3 . The intercalated pyridine molecules increase the separation distance between the Bi_2Se_3 quintuple layers (QLs), suppressing the parity inversion of the electronic states at the Γ -point. We find that the intercalated region becomes a trivial insulator. By combining the pristine Bi_2Se_3 region with the one intercalated by the molecules, we have a non-trivial/trivial heterojunction characterized by the presence of (topologically protected) metallic states at the interfacial region. Next we apply an external compressive pressure to the system, and the results are (i) a decrease on the separation distance between the QLs intercalated by pyridine molecules, and (ii) the metallic states are shifted toward the bulk region, turning the system back to insulator. That is, through a suitable tuning of the external pressure in Bi_2Se_3 , intercalated by pyridine molecules, we can control its topological properties; turning-on and -off the topologically protected metallic states lying at the non-trivial/trivial interface.

Three dimensional topological insulators (TIs) are insulator materials in the bulk phase, but they present metallic topological surface states (TSSs), which are protected by time-reversal symmetry; as a result backscattering processes by time-reversal invariant impurities or defects are forbidden¹. These materials are of great promise for spintronics applications, due to the formation of nearly dissipationless spin-polarized surface current². Currently, Bi_2Se_3 is one of the most investigated TI due to its large band gap (~ 0.3 eV), nearly idealized single Dirac cone and for being a pure compound³⁻⁵. Bi_2Se_3 presents a rhombohedral structure composed by quintuple layers (QLs) of Se and Bi atoms, forming a sequence of Se-Bi-Se-Bi-Se atoms covalently bonded; these QLs are stacked along the c -axis of a hexagonal structure by van der Waals (vdW) interactions.

Recent experiments have been exploring the possibility of inserting guest species in the vdW gaps of Bi_2Se_3 , this process is known as intercalation. Koski *et al.*^{6,7} have added various zerovalent metals in the vdW gaps of Bi_2Se_3 nanoribbons, it is expected that new properties and/or tuning of the Bi_2Se_3 properties can be achieved by intercalation, e.g. superconductivity⁸. Beside metals, molecules have been intercalated in Bi_2Se_3 , for instance, it has been shown that pyridine molecules in Bi_2Se_3 present interesting properties for optoelectronic applications⁹.

In this work we aim to investigate the geometry and electronic structure of Bi_2Se_3 intercalated by pyridine molecules (py- Bi_2Se_3). Upon the presence of the pyridine molecules between the QLs, we find that the py- Bi_2Se_3 system becomes a trivial insulator. By considering a heterojunction composed by py- Bi_2Se_3 and pristine Bi_2Se_3 (py- $\text{Bi}_2\text{Se}_3/\text{Bi}_2\text{Se}_3$), we analyze (i) the occurrence

of topologically protected metallic states embedded in py- $\text{Bi}_2\text{Se}_3/\text{Bi}_2\text{Se}_3$, and (ii) the control of those metallic states (turning-on and -off) upon the application of external pressure.

The calculations are performed based on the density-functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP)¹⁰. We use the generalized gradient approximation (GGA), in the form proposed by Perdew, Burke and Ernzerhof¹¹, to describe the exchange-correlation functional. The Kohn-Sham orbitals are expanded in a plane wave basis set with an energy cutoff of 400 eV. The electron-ion interactions are taken into account using the Projector Augmented Wave (PAW) method¹². All geometries have been relaxed until atomic forces were lower than 0.02 eV/Å. The Brillouin Zone is sampled according to the Monkhorst-Pack method¹³, using at least a $3 \times 3 \times 1$ mesh. We have also used a functional that accounts for dispersion effects, representing van der Waals (vdW) forces, according to the method developed by Tkatchenko-Scheffler (TS)¹⁴, which is implemented on VASP¹⁵. The inclusion of van der Waals forces in the simulations is necessary to obtain the correct vdW gap between two QLs¹⁶, the interaction between molecule and Bi_2Se_3 is also better described with the inclusion of vdW interactions.

Initially we calculate the equilibrium distance (z_0) between two consecutive QLs of Bi_2Se_3 , vdW gap. Here we have considered two isolated QLs and minimize the total energy as a function of the width of vdW gap (Δz)¹⁷. As shown in Fig. 1 (squares), we find the energy minimum for $z_0 = 2.65$ Å; this result is in agreement with experimental measurements¹⁸, and recent theoretical studies^{16,19}. By using the same procedure, we determine z_0 upon the presence of a pyridine molecule intercalated in between the QLs. The QLs present a 2×2 surface periodicity, which corresponds to a molecular concentration of 1.64×10^{-2} mol./Å². In this case, we find that (i) there

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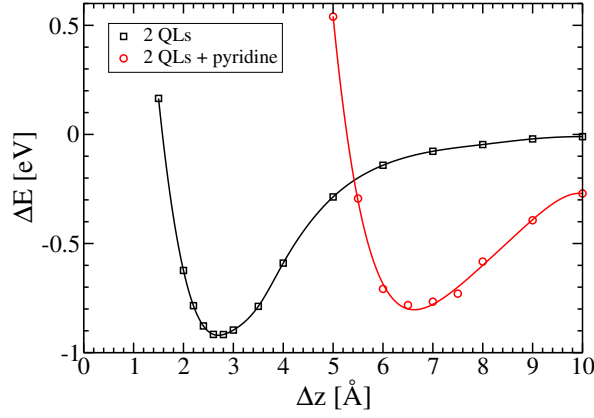


FIG. 1. Formation energy for two Bi_2Se_3 QLs at various separation distances. Black line (circles) represents the pristine system and red line (squares) the system with a pyridine molecule intercalated between the 2 QLs.

is no chemical bonding between the molecule and the Bi_2Se_3 QLs, and (ii) the vdW gap increases by 3.85 \AA , $z_0 = 2.65 \rightarrow 6.50 \text{ \AA}$, Fig. 1 (circles). Such an increase of the vdW gap reduces the binding energy between the QLs, however, the formation of pyridine intercalated Bi_2Se_3 QLs is still an exothermic process.

TIs present a parity inversion between valence and conduction bands due to spin-orbit coupling (SOC). For Bi_2Se_3 the bulk phase presents a band parity inversion at the Γ -point, namely the SOC induces a band inversion between Se p_z -orbitals in the valence band and Bi p_z -orbitals in the conduction band³. We use this characteristic to determine whether the material is behaving as trivial or topological insulator. Thus, by turning-off the SOC, we observe that higher energy levels of the valence band have higher contribution from the Se p_z -orbitals, while the lower energy levels of the conduction band are dominated by Bi p_z -orbitals. Meanwhile, by turning-on the SOC we observe an inversion between valence and conduction band orbitals around the Γ -point, promoting the (band) parity inversion. The same procedure was applied to examine if such a band inversion still occurs in py- Bi_2Se_3 . By considering the pyridine concentration of $1.64 \times 10^{-2} \text{ mol./\AA}^2$ intercalated in Bi_2Se_3 , we verify that when the SOC is not included the py- Bi_2Se_3 system is an insulator, where the valence band maximum is dominated by Se p_z -orbitals and the conduction band minimum by Bi p_z -orbitals [Fig. 2(a)], as observed for the pristine Bi_2Se_3 bulk. In contrast, by turning SOC on we observe the lack of band inversion around the Γ -point [Fig. 2(b)], suggesting that pyridine molecules intercalated in Bi_2Se_3 bulk suppress its topological properties, namely, the py- Bi_2Se_3 system is a trivial insulator.

This topological-trivial transition in the Bi_2Se_3 structure is possibly caused by the increase in the vdW gaps due to the pyridine intercalation. In order to verify such an assumption, we calculate the electronic band structure of Bi_2Se_3 , but keeping the equilibrium geometry of

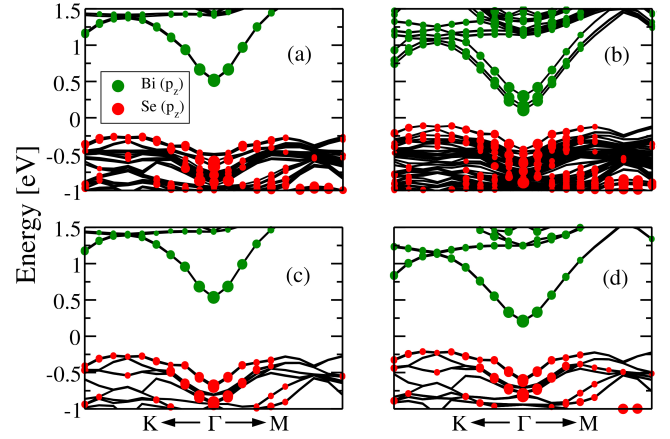


FIG. 2. Band structures for (a) Bi_2Se_3 bulk with intercalated pyridine molecules excluding SOC, and in (b) including SOC. (c) Bi_2Se_3 bulk with the vdW gap obtained in the system with intercalated molecules (Fig. 1), excluding SOC; and in (d) including SOC. The symbols are contributions of p_z -orbitals for Se (red) and Bi (green) atoms.

the pyridine intercalated Bi_2Se_3 system. Our results are presented in Figs. 2(c) and 2(d), by turning-off and -on the SOC we observe that the band inversion at the Γ -point is still absent.

In experiments we would most likely observe regions with pyridine molecules intercalated between the vdW gaps and regions of pristine Bi_2Se_3 , as a result we may have a trivial/topological insulator heterojunction composed by py- Bi_2Se_3 and Bi_2Se_3 (py- $\text{Bi}_2\text{Se}_3/\text{Bi}_2\text{Se}_3$). To simulate such a heterojunction, we have considered a supercell containing 9 QLs, where we have three QLs intercalated by the molecules and six consecutive pristine QLs, $(\text{py-Bi}_2\text{Se}_3)_3/(\text{Bi}_2\text{Se}_3)_6$. As shown in Fig. 3, the pyridine molecules are intercalated between QL(1) and QL(4), characterizing the $(\text{py-Bi}_2\text{Se}_3)_3$ region, and QL(4)/QL(5)/.../QL(9)/QL(1) forms the pristine $(\text{Bi}_2\text{Se}_3)_6$ region. Given that geometry, the trivial/topological interface are characterized by QL(1) and QL(4). Band structure calculations reveal the presence of metallic states forming a Dirac-like cone at the Γ -point, indicated by solid black lines in Fig. 3. To localize these states we compute the p_z -orbitals contribution from various QLs around the Γ -point, and project these states in the energy levels shown in the band structure²⁰. We find that the electronic states around the Dirac point are mainly attributed to the Bi p_z -orbitals lying at the py- $\text{Bi}_2\text{Se}_3/\text{Bi}_2\text{Se}_3$ interface region, QL(1) and QL(4). In contrast, there are no electronic contribution to the metallic states from the py- Bi_2Se_3 bulk region, QL(2) and QL(3). Somewhat similarly, the electronic contributions to the Dirac-like cone coming from the bulk region of Bi_2Se_3 [QL(5)–QL(8)] are almost negligible. Those findings allow us to conclude that $(\text{py-Bi}_2\text{Se}_3)_m/(\text{Bi}_2\text{Se}_3)_n$ heterostructures (or superlattices) give rise to topologically protected metallic states, em-

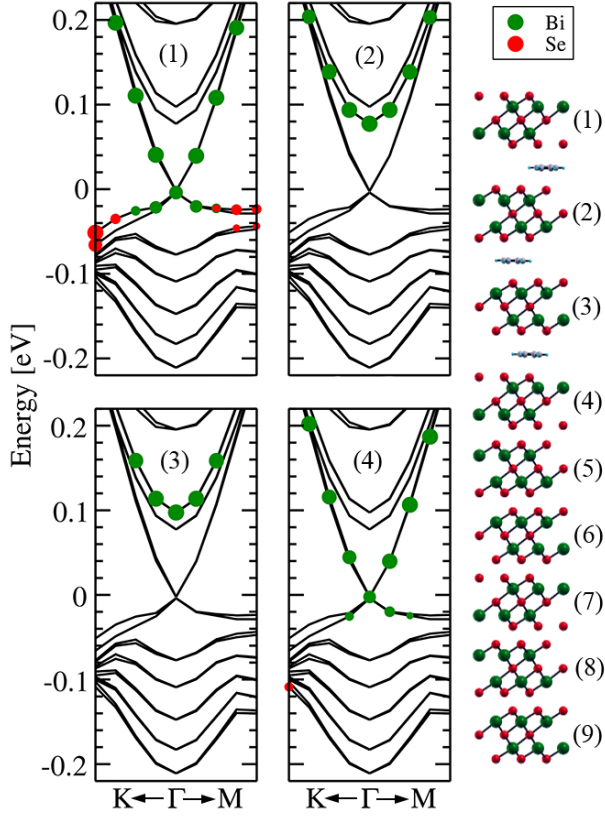


FIG. 3. Each panel shows the band structure (full black lines) for the structure shown on the right side. The p_z -orbital states is projected on the band structure for the first four QLs, where green circles represent Bi p_z -orbitals and red circles Se p_z -orbitals.

bedded at the trivial/topological interface region. However, it is worth noting that the appearance of those topologically protected surfaces states depends on the topological film (Bi_2Se_3) thickness (n). In Ref. ²¹ the authors verified the presence of converged TSS for 3 QLs of Bi_2Se_3 . On the other hand, in a recent study, we verify the formation of TSSs for an interlayer spacing, *i. e.* vdW gap, larger than $\sim 5.5 \text{ \AA}$ ²². Thus, we can infer that it is possible to get topologically protected metallic channels by considering just a single layer of py- Bi_2Se_3 embedded in Bi_2Se_3 .

In order to verify the statement above, we construct a supercell containing one molecule separated by six Bi_2Se_6 QLs, $(\text{py-Bi}_2\text{Se}_3)_1/(\text{Bi}_2\text{Se}_6)_5$, this structure is shown in Fig. 4 (c). Indeed, we find the TSSs forming a Dirac-like cone at the Γ -point, as shown in Fig. 4 (a). Those states lie at the $(\text{py-Bi}_2\text{Se}_3)_1/(\text{Bi}_2\text{Se}_3)_5$ interface region. The spin-texture of TSSs is constrained by the time reversal symmetry. Here we calculate the expected value of spin-polarization components ($\langle S_n(\mathbf{k}) \rangle$) for the TSSs, of $(\text{py-Bi}_2\text{Se}_3)_1/(\text{Bi}_2\text{Se}_3)_5$, near the Dirac point. $\langle S_n(\mathbf{k}) \rangle$ can be written as $\langle S_{n,\alpha}(\mathbf{k}) \rangle = (\hbar/2) \langle \phi_n(\mathbf{k}) | \sigma_\alpha | \phi_n(\mathbf{k}) \rangle$, in cartesian coordinates ($\alpha = x, y, z$), where σ represents

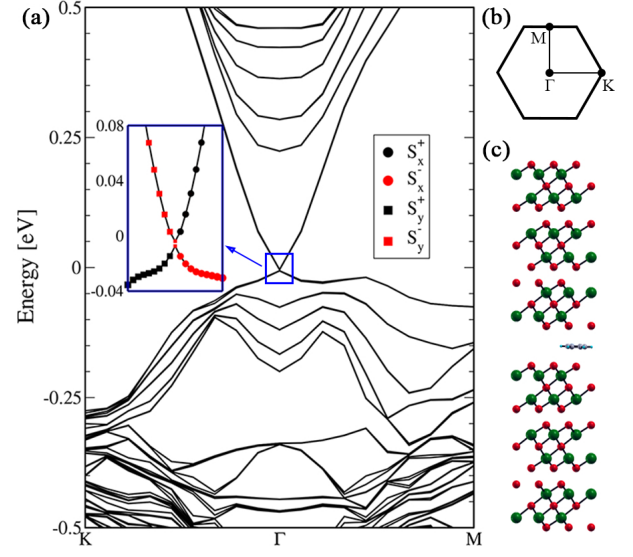


FIG. 4. (a) Band structure for the system depicted in (c), along the path shown in the projected surface 2D Brillouin zone represented in (b). The inset in (a) shows the spin-texture inside the blue square region around the Γ -point.

the Pauli matrices, and $\phi_n(\mathbf{k})$ the single particle Kohn-Sham eigenfunction, and n represents the band index. We have considered $\phi_n(\mathbf{k})$ for wave vectors (\mathbf{k}) along the Γ -M and Γ -K directions. As depicted in the inset of Fig. 4(a), for the electronic states parallel to the Γ -M direction, we find (i) positive (negative) values of $\langle S_{n,x}(\mathbf{k}) \rangle$ for the occupied (empty) states, while (ii) $\langle S_{n,z}(\mathbf{k}) \rangle = \langle S_{n,y}(\mathbf{k}) \rangle = 0$; whereas for \mathbf{k} parallel to the Γ -K direction, we find (iii) negative (positive) values of $\langle S_{n,y}(\mathbf{k}) \rangle$ for the occupied (empty) states, (iv) $\langle S_{n,x}(\mathbf{k}) \rangle = 0$, and (v) $\langle S_{n,z}(\mathbf{k}) \rangle$ values are negligible around the Γ -point. Such a picture of $\langle S_{n,\alpha}(\mathbf{k}) \rangle$, for the TSSs lying at the $(\text{py-Bi}_2\text{Se}_3)_1/(\text{Bi}_2\text{Se}_3)_5$ interface, is practically the same as that obtained for the TSSs on the $\text{Bi}_2\text{Se}_3(111)$ surface ^{21,23}.

We now propose a mechanism to gain control over the topologically protected metallic states in $(\text{py-Bi}_2\text{Se}_3)_m/(\text{Bi}_2\text{Se}_3)_n$. In particular, we considered the $(\text{py-Bi}_2\text{Se}_3)_1/(\text{Bi}_2\text{Se}_3)_5$ system. We apply a compressive pressure directed along the c -axis, namely normal to the QLs, decreasing the separation distance in the vdW gap (Δz) from 6.50 \AA to 4.12 \AA , upon an external pressure of $P \approx 9.1 \text{ GPa}$. This (pressure) value is comparable to the ones achieved experimentally for Bi_2Se_3 structures ^{24,25}. The energy difference between the relaxed and compressed $(\text{py-Bi}_2\text{Se}_3)_1/(\text{Bi}_2\text{Se}_3)_5$ is shown in the upper part of Fig. 5. An energy of $\sim 10 \text{ meV/\AA}^2$ needs to be added to compress the system from $\Delta z = 6.50$ to 4.12 \AA . In the lower part of Fig. 5 we show the band structure for four values of Δz , starting from 6.50 \AA which has already been shown to have metallic states. For $\Delta z = 5.65 \text{ \AA}$, the metallic states at the Γ -point are still present. Upon further decrease of Δz , the metallic states start to move in the bulk band direction. For Δz

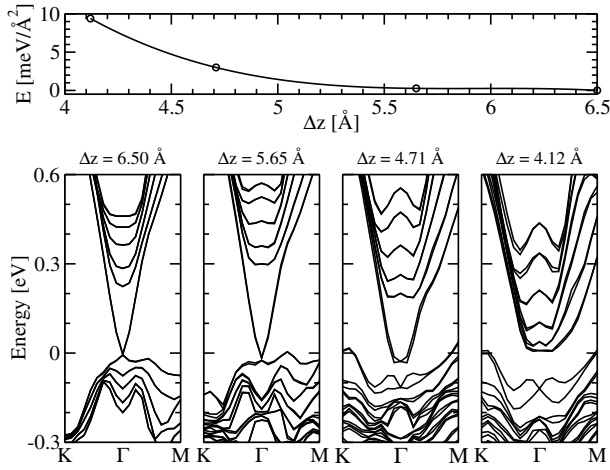


FIG. 5. *Upper panel:* Energy per area to compress the relaxed structure shown in Fig. 4 (c), reducing the vdW gap between the QLs separated by the molecule. *Lower panels:* Band structure for the various Δz values.

= 4.71 Å, the Dirac point has been suppressed, as we find an energy gap at the Γ -point. The energy gap at the Γ -point is even larger for $\Delta z = 4.12$ Å, washing out the TSSs at the $(\text{py-Bi}_2\text{Se}_3)_1/(\text{Bi}_2\text{Se}_3)_5$ interface region. By removing the pressure the system can reversibly return to its original geometry, and again the metallic states will be present. Thus, we can combine pressure application and pyridine molecules intercalation to the Bi_2Se_3 structure to turn the topologically protected metallic states on and off, going from an insulator to a semi-metallic material by taking advantage of the TI properties of Bi_2Se_3 . The results presented above can be extended to any number of QLs intercalated by molecules, assuring that we have a $\text{Bi}_2\text{Se}_3/\text{py-Bi}_2\text{Se}_3$ junction.

We have performed an *ab initio* study of pyridine molecules intercalated in the vdW gaps of Bi_2Se_3 ($\text{py-Bi}_2\text{Se}_3$). In $\text{py-Bi}_2\text{Se}_3$ the inter-QL distance increases, which turns the TI material into a trivial insulator. By considering $(\text{py-Bi}_2\text{Se}_3)_m/(\text{Bi}_2\text{Se}_3)_n$ heterojunctions, we find a trivial/topological interface, characterized by the presence of topologically protected metallic states (forming a Dirac-like cone) embedded at the interface region of the heterostructure. Such metallic states can be present even for a single QL incorporated by pyridine molecules, $(\text{py-Bi}_2\text{Se}_3)_1/(\text{Bi}_2\text{Se}_3)_n$. Lastly, we have shown the possibility to control the occurrence of such metallic states in $(\text{py-Bi}_2\text{Se}_3)_m/(\text{Bi}_2\text{Se}_3)_n$, upon an external compressive strain; turning-on and -off those metallic states at the heterojunction interface.

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